"Nano-ice" Forms in Cold Water and Causes the Density Maximum Anomaly

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Summary: Small size (a few nm) ice crystallite, "Nano-ice", forms in cold water below 10 °C. Its formation impedes the increase of density during cooling down and makes a maximum at 4 °C. COLD WATER IS NOT A GENUINE LIQUID.

Introduction: Water is still mysterious despite intensive and extensive studies over the years. Anomalous behaviour of water as a liquid is yet to be fully comprehended. Here we show that the most generally known anomaly of water, the density maximum anomaly, is well accounted for by the formation of "Nano-ice" at low temperatures.

Results and Discussion: We observed 140 Raman spectra of water in the temperature range -23 °C~45°C [1]. Spectra in the temperature range 15~45°C show clear iso-scattering points. The multivariate curve resolution with alternate least-squares (MCR-ALS) method [2] yields two spectral components corresponding to the two forms of water, Forms A and B (Fig. 1(a)). Form A does not show any clear intermolecular bands in the low-wavenumber region, while Form B shows two distinct bands. Forms A and B are identified as de-structured and structured hydrogen-bonded waters, respectively. In addition to Forms A and B, another form of water (Form C) coexists in the lower temperature range of −23°C ~0°C. Hypothetical addition multivariate analysis with numerical differentiation (HAMAND) analysis [3] extracts the third spectral component corresponding to Form C. The spectrum of Form C obtained at -23°C resembles that of ice. From the temperature dependent fractions of Forms A, B and C (Fig. 1(b)), we are able to simulate the temperature dependence of water density. Assuming that the density of Form C is the same as that of ice I_h, the simulation successfully reproduces the temperature dependence with a maximum at the right temperature (Fig. 1(c)). Mystery of density maximum of water has thus been given an unequivocal solution. Form C identified as small size ice crystallite might well be called "Nano-ice" (Fig. (d)).
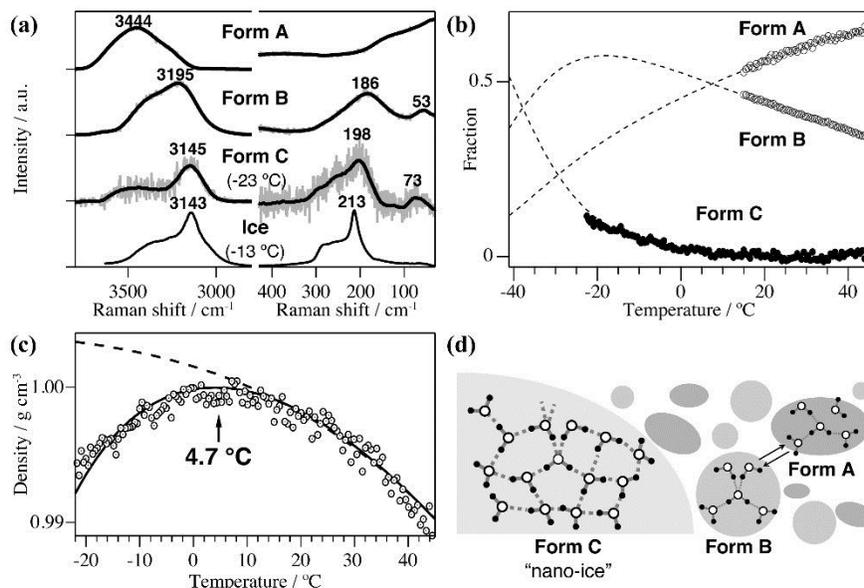

Figure 1. (a) Raman spectra of Forms A, B, C at -23 °C, and that of ice at -13 °C. (b) Temperature dependent fractions of Forms A, B and C. (c) Estimated water density (open circles) with the observed (solid line). (d) Conceptual illustration of the three forms of water; Form A, destructured hydrogen-bonded water, Form B, structured hydrogen-bonded water and Form C, "nano-ice".

Raman band shapes of small particles are sensitive to their sizes. In order to extract size information for "Nano-ice", we adopt the phonon confinement model (PCM, [4]). We start with a DFT calculation of the dispersion $\omega_i(q)$ of the i-th phonon mode of ice and the differential intensity $A_i(q_0, \varphi, \theta)$ for the scattering angle φ, ϑ, where q is the wave vector of the Brillouin zone with q_0 being the wave vector of the bulk crystal. Assuming a spherical phonon confinement, we then obtain the Fourier coefficients $C(q_0, q)$ in the form of Bessel-like function. $C(q_0, q)$ corresponds to the expansion coefficient of the confined phonon wave function into a linear combination of the bulk phonon wave functions. It represents how the Raman intensities of bulk phonon at q_0 are distributed into different wave vector q of the confined phonon. The Raman intensity $I(\omega)$ at wavenumber ω is given by the following equation;

$$I(\omega) \cong \sum_i \iiint \frac{A_i(q_0, \varphi, \theta) * \Gamma_{0,i} * |C(q_0, q)|^2 * q^2}{(\omega - \omega_i(q))^2 + (\Gamma_{0,i}/2)^2} dq\, d\varphi\, d\theta \; ,$$

where $\Gamma_{0,i}$ is the natural linewidth and q is the norm of q.

The observed spectra of Forms A, B, C and ice are compared with the PCM simulated spectra in Figure 2. The PCM simulation well reproduces the observed Raman spectra of Forms B and C. Note that the calculated wavenumbers and intensities of ice are scaled to match the experimental spectrum. The results indicate that the size of "nano-ice" is most likely to be a few nm and that Form B corresponds nicely to the unit cell (u.c.) of the tetrahedral structure of ice.
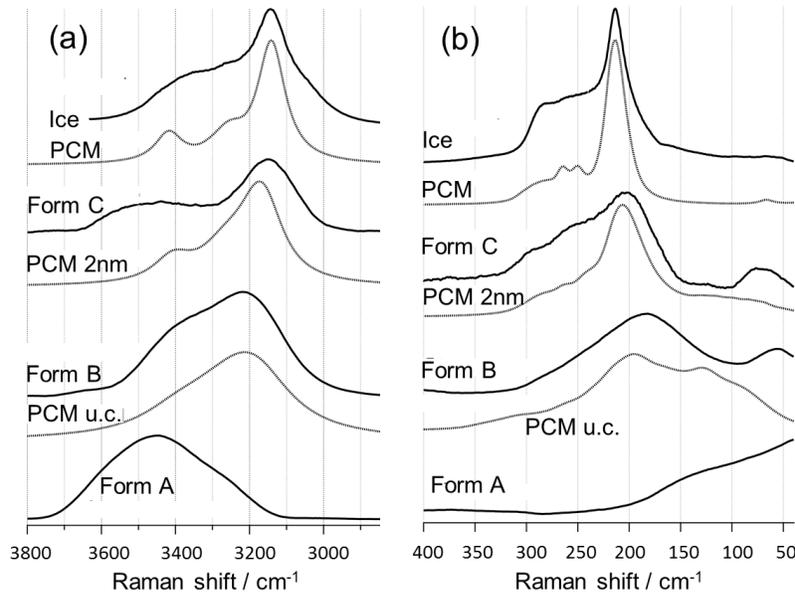
Figure 2. Comparison of the observed (full line) and PCM simulated (dotted line) Raman spectra of water and ice.
(a) High wavenumber region. (b) Low wavenumber region.

Conclusion: Raman hyperspectroscopy has solved water mystery by showing the formation of "Nano-ice" in cold water below 10 °C. It causes the density maximum anomaly of water. Cold water is not a genuine liquid.

References:
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